II.A Distributed Production Technologies

II.A.1 Ceramic Membrane Reactor Systems for Converting Natural Gas to Hydrogen and Synthesis Gas (ITM Syngas)

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Objectives

- Research, develop and demonstrate the ITM Syngas ceramic membrane reactor system for the low-cost conversion of natural gas to hydrogen and synthesis gas.
- Scale up the ITM Syngas reactor technology through three levels of pilot-scale testing and precommercial demonstration.
- Obtain the technical, engineering, operating and economic data necessary for the final step to full commercialization of the ITM Syngas technology.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- A. Fuel Processor Capital Costs
- D. Carbon Dioxide Emissions
- AA. Oxygen Separation Technology

(This project also addresses DOE Office of Fossil Energy objectives to develop lower-cost methods to produce hydrogen from natural gas.)

Approach

This project is in Phase 2 of three phases. The approach in Phase 2 includes the following tasks:

- Task 2.1 Commercial Plant Economic Evaluation

- Task 2.2 Materials and Seals Development and Evaluation
- Task 2.3 ITM Syngas Membrane and Module Design and Fabrication
- Task 2.4 Nominal 24,000 SCFD ITM Syngas Process Development Unit (PDU)
- Task 2.5 Nominal 330,000 SCFD ITM Syngas Subscale Engineering Prototype (SEP)

Accomplishments

- Fabricated a multi-membrane module with hermetically sealed all-ceramic joints.
- Fabricated commercial-size ceramic membranes and SEP module components.
- Operated the pilot-scale Process Development Unit (PDU) at its design capacity of 24 MSCFD.
- Achieved target oxygen flux in the PDU with pilot-scale membranes.
- Projected costs for a distributed-scale hydrogen process (860 kg/day hydrogen, 100 units/year) of $1.56/kg of hydrogen for reforming plus purification (25% below DOE target for 2005).

Future Directions

- Test catalyzed planar membranes in PDU.
- Initiate tests to validate commercial-size membrane design.
- Fabricate integrated subscale membrane module of commercial-size planar membrane.
- Test subscale module of commercial-size planar membrane.
- Demonstrate performance of commercial-size planar membrane that meets economic targets at commercial conditions.
- Initiate engineering design of the SEP plant.

Introduction

Ion transport membranes (ITMs) are a revolutionary platform technology for producing hydrogen and synthesis gas for applications in power generation, transportation fuels, and chemicals. The ITM Syngas process provides a lower-cost method for converting natural gas to hydrogen and synthesis gas by combining air separation and natural gas partial oxidation in a single-step ceramic membrane reactor, with the potential for capital cost savings of over 30%. When successful, this technology will be important to emerging hydrogen markets, such as hydrogen-based fuel cells for transportation and centralized hydrogen production facilities with carbon dioxide capture.

ITM ceramic membranes are fabricated from non-porous, multi-component, metallic oxides and operate at high temperatures with exceptionally high oxygen flux and selectivity. A conceptualization of the ITM Syngas technology is shown in Figure 1. Oxygen ions from low-pressure air permeate the ceramic membrane and are consumed through chemical reactions, creating a chemical driving force that pulls oxygen ions across the membrane at high rates. The oxygen reacts with natural gas in a partial oxidation process to produce a hydrogen and carbon monoxide mixture (synthesis gas).

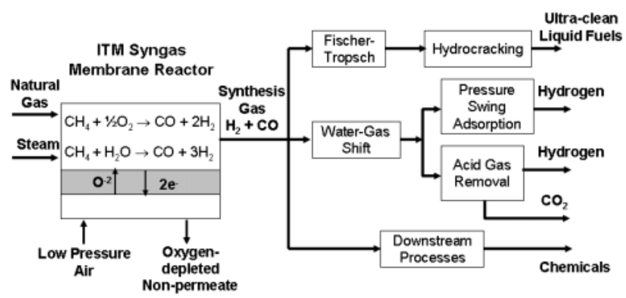

Figure 1. Conceptual ITM Syngas Process with Several Applications

Approach

The objective of this project is to research, develop and demonstrate a novel ceramic membrane reactor system for the low-cost conversion of natural gas to hydrogen and synthesis gas: the ITM Syngas

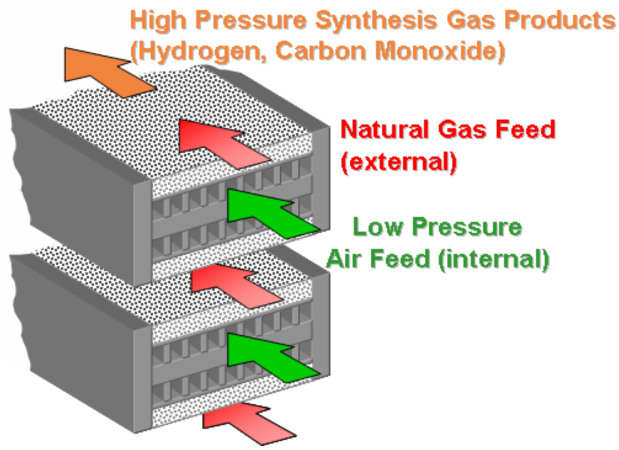

Figure 2. ITM Syngas Ceramic Membrane Module Diagram

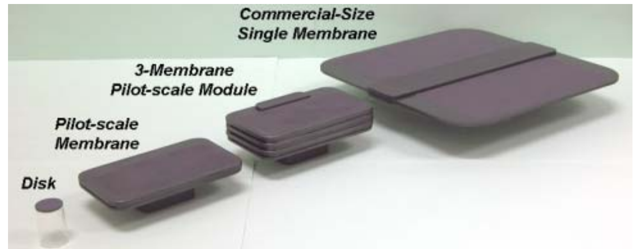

Figure 3. Advances in Scaling Up ITM Syngas Ceramic Membranes

process. Through a 9½-year, three-phase project, the ITM Syngas technology will be developed and scaled up to obtain the technical, engineering, operating and economic data necessary for the final step to full commercialization of the hydrogen- and synthesis gas-generation technology.

In Task 2.1, "Commercial Plant Economic Evaluation," advanced ITM Syngas processes will be developed, and the economics of operation at the commercial-plant scale will be evaluated based on the results of Phase 2. In Task 2.2, "Materials and Seals Development and Evaluation," membrane materials and seals will be tested at the laboratory scale under process conditions to obtain statistical performance and lifetime data. In Task 2.3, "ITM Syngas Membrane and Module Design and Fabrication," membrane reactors will be designed for the ITM Syngas process at the PDU, SEP and commercial scales. Pilot-scale membrane modules will be fabricated for testing in the PDU, and fabrication of the membrane reactor modules will be scaled up in a Production Development Facility to supply the requirements of the SEP.

In Task 2.4, "Nominal 24,000 SCFD ITM Syngas PDU," the components of the ITM Syngas technology will be demonstrated in a laboratory PDU. The PDU will operate at an equivalent of 24,000 SCFD of synthesis gas capacity and will performance test pilot-scale planar membranes under commercial process conditions. In Task 2.5, "Nominal 330,000 SCFD ITM Syngas SEP," a SEP unit will be built to demonstrate the ITM Syngas technology using commercial-size membranes in subscale modules. The SEP will demonstrate the operation of the ITM Syngas process at up to an equivalent of 330,000 SCFD synthesis gas capacity.

Results

A microchannel planar membrane design (Figure 2) was developed in Phase 1 and was selected over tubular membrane designs. The microchannel passages allow the planar membrane to achieve high rates of heat and mass transfer. Membrane fabrication has progressed quickly through the use of scalable fabrication processes. The first planar articles were small disks (Figure 3). Next, rectangular pilot-scale membranes were fabricated that included all the critical engineering features found in commercial-scale wafers, thereby providing an excellent subscale surrogate for the development of commercial-size wafer fabrication processes. Fabrication of commercial-size wafers was initiated in 2003. These represent a 300-fold increase in module area from the first planar membranes fabricated in 1999.

An ITM module can be created by stacking wafers vertically. The sample ITM module in Figure 3 shows a 3-wafer module built from pilot-scale membranes. The wafers were joined and sealed to ceramic spacers that create an open channel for the flow of natural gas and synthesis gas between wafers (Figure 2). The use of an all-ceramic sealant to join the ceramic parts is a key enabling technology. The sealant and the membranes are of a uniform material in order to match the expansion behavior of the components and reduce stresses in the module.

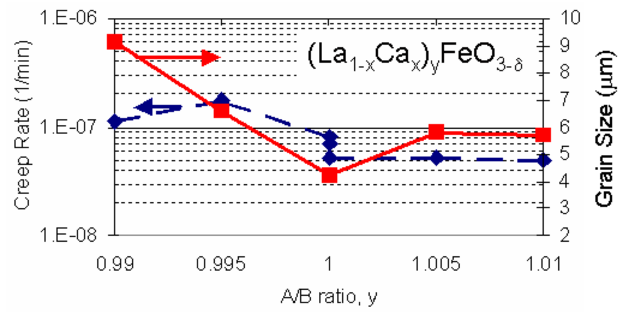

Figure 4. Creep Rate as a Function of A/B Cation Ratio, y

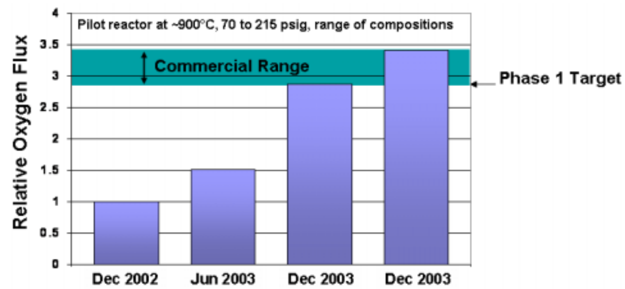

Figure 5. Advances in Oxygen Flux Measured in Process Development Unit

The ITM Syngas process places severe demands on the membrane material. The membrane must simultaneously meet the following criteria:

- It must be thermodynamically stable in the high-pressure, reducing natural gas feed and in the intermediate synthesis gas.
- It must be thermodynamically stable in the low-pressure, oxidizing air feed.
- It must have sufficient mixed electronic and oxygen ion conductivity to achieve economically attractive oxygen fluxes.
- It must have the requisite mechanical properties (strength, creep, and expansion) to meet lifetime and reliability criteria.

Through the careful tailoring of the membrane composition, a patented family of materials [1] developed by the ITM Syngas team meets these criteria.

The economics of syngas production look most attractive when a high-pressure natural gas feed and a low-pressure air feed are used to produce a high-pressure synthesis gas product to match downstream process pressures, thus avoiding the expenses associated with compressing the air. A large hydrostatic pressure difference will exist across the membrane from the synthesis gas side to the air side of the membrane. To achieve the required long service life, the membrane material will have to have a sufficiently low creep rate at process temperatures to avoid excessive creep deformation or creep rupture of the membrane.

The family of materials that has been carefully designed to meet this condition consists of perovskites with the formula $(La_{1-x}Ca_x)_yFeO_{3-\delta}$, where $0<x<0.5$; $1.0<y$ and δ make the compound charge neutral. The A/B cation ratio, y, has a large effect on the observed creep rates; dense 50 x 4 x 2 mm bars of $(La_{1-x}Ca_x)_yFeO_{3-\delta}$ were prepared where y=0.98, 0.99, 1.00, 1.01 and 1.02 and x was maintained constant. Figure 4 shows the 4-point bending creep rate as a function of the A/B ratio, y, along with the grain size of the samples. The creep rate decreases by a factor of 2 as the A/B ratio increases from less than 1.0 to greater than 1.0. This observation is even more impressive when one considers that the creep rate can increase significantly with decreasing grain size. The samples (A/B ratio of y >1.0) with the lowest creep rates had a much smaller grain size than the samples (y <1.0) with the highest creep rates. Therefore, lower creep rates and longer membrane life can be obtained by using A/B ratios greater than 1.0.

A PDU constructed at Air Products is used to test pilot-scale planar membranes at full process operating conditions. The PDU demonstrated a design capacity of 24 MSCFD synthesis gas and is suitable for testing both pilot- and full-size membranes.

Recent PDU tests with pilot-size membranes included operation under synthesis gas conditions at temperatures between 800 and 900°C and pressures between 215 and 425 psig. Membranes demonstrated the ability to operate and remain intact through changes in temperature, pressure, and gas composition. Pilot-scale membranes tested in the PDU have demonstrated the target oxygen flux (Figure 5), representing a factor of three increase in flux measured in the PDU since 2002. These increases in flux were achieved through a combination of membrane and reactor design refinements and improvements in PDU operation. Improved designs in the PDU have dramatically reduced contaminants from process system materials of construction.

A design was developed for a distributed-scale hydrogen generation system to produce 860 kg/day of hydrogen. The economic evaluation followed the basis outlined in the 2003 DOE Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan. The cost of hydrogen from an ITM Syngas reformer coupled with a pressure swing adsorption unit was projected to be $1.56/kg of hydrogen, which is 25% below the DOE 2005 target of $2.09 for this scope. ITM Syngas is a step-change technology, and additional cost reductions should be possible with further development.

Conclusions

Significant progress has been made in materials selection, membrane design and fabrication, and catalyst development, which are necessary steps toward commercializing the ITM Syngas technology. These advancements have led to successful demonstration of the technology in the Process Development Unit. The potential economic benefits of the technology continue to be very promising.

References

1. P.N. Dyer, M.F. Carolan, D. Butt, R.H.E. VanDoorn, and R.A. Cutler, "Mixed Conducting Membranes for Syngas Production," U.S. Patent No. 6492290 B1 (2002).

FY 2004 Publications/Presentations

1. "Development of the ITM Syngas Ceramic Membrane Technology,"AIChE Spring National Meeting, New Orleans, LA, April 26, 2004.
2. "ITM Syngas Ceramic Membrane Technology for Synthesis Gas Production," 7th Natural Gas Conversion Symposium, Dalian, China, June 6-10, 2004.
3. "Hydrogen and Syngas Production Using Ion Transport Membranes," 8th International Conference on Inorganic Membranes, Cincinnati, OH, July 18-21, 2004.

FY 2004 Patents/Applications

1. A patent application covering reactor vessel design was filed.